

PCT

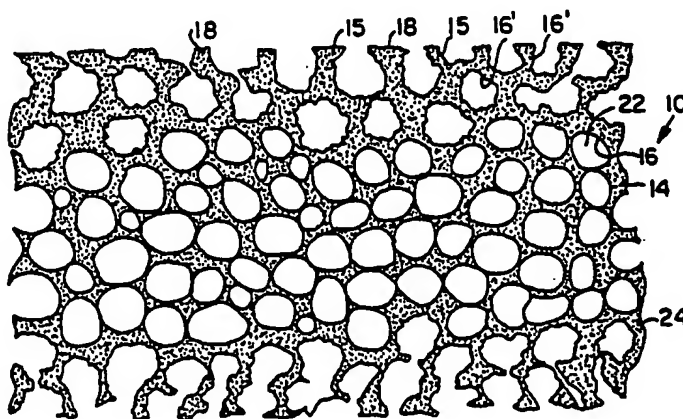
WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>5</sup> : C08J 5/14, C09K 3/14 H01L 21/304, 21/463, 29/34 B05D 1/12, 3/10, 3/12 B32B 3/20, 3/30</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 94/04599</b>  (43) International Publication Date: 3 March 1994 (03.03.94)</p>
<p>(21) International Application Number: PCT/US93/07256 (22) International Filing Date: 2 August 1993 (02.08.93)  (30) Priority data: 932,161 19 August 1992 (19.08.92) US  (71) Applicant: RODEL, INC. [US/US]; Diamond State Industrial Park, 451 Bellevue Road, Newark, DE 19713 (US).  (72) Inventors: REINHARDT, Heinz, F. ; 19 McCarthy Road, Chadds Ford, PA 19317 (US). ROBERTS, John, V., H. ; 17 West Country Lane, Newark, DE 19702 (US). McCLAIN, Harry, George ; 257 Sugarpine Drive, Middletown, DE 19709 (US). JENSEN, Elmer, William ; 325 South DuPont Highway, New Castle, DE 19720 (US). BUDINGER, William, D. ; 451 Bellevue Road, Newark, DE 19713 (US).</p>	<p>(74) Agents: NADEL, Alan, S. et al.; Panitch Schwarze Jacobs &amp; Nadel, 1601 Market Street, 36th Floor, Philadelphia, PA 19103 (US).  (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BI, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.</p> <p><b>BEST AVAILABLE COPY</b></p>	

(54) Title: POLYMERIC SUBSTRATE WITH POLYMERIC MICROELEMENTS



(57) Abstract

The present invention relates to an article of manufacture or polishing pad (10) for altering a surface of a workpiece, such as polishing or planarizing a semiconductor device. The article includes a polymeric matrix (14) impregnated with a plurality of polymeric microelements (16), each polymeric microelement having a void space (22) therein. The article has a work surface (18) and a subsurface proximate to the work surface. When the article is in contact with a working environment, polymeric microelements (16) at the work surface of the article are less rigid than polymeric elements embedded in the surface. As the work surface of the article is abraded during use, the work surface of the pad may be continuously regenerated. In alternative preferred embodiments, the work surface may further include a minitexture and/or a macrotexture.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

- 1 -

## 5 POLYMERIC SUBSTRATE WITH POLYMERIC MICROELEMENTS

Field of the Invention

The invention relates to a polymeric substrate impregnated with polymeric microelements  
10 and methods of making and using the same and, more particularly, to an article of manufacture for use in polishing materials, such as semiconductor devices.

Background of the Invention

15 Conventional polymeric substrates or polishing pads used for polishing, planarizing and other operations for which the present article is useful may be subjected to a variety of operating conditions which influence the selection of the  
20 substrate material. For example, variations in the nature of the workpiece being polished, polishing speed and pressure, elevated temperatures generated during the polishing operation, and the nature of any polishing slurry used in the operation may  
25 influence the choice of substrates.

Conventional polymeric polishing pads often vary in quality due to imprecise control of polymerization and blending processes and cutting and shaping of the final pad product. Therefore,  
30 the polishing characteristics imparted to a

- 2 -

workpiece being polished, such as surface quality, stock removal rate and planarization rate, typically vary greatly between pad batches.

Conventional polishing pads are generally  
5 formed from multilayer laminations or stratified substrates having non-uniform physical properties throughout the thickness of the pad. An example of a typical stratified pad widely used for polishing semiconductor devices is the Politex Supreme pad,  
10 which is commercially available from Rodel Incorporated, of Newark, Delaware. A typical Politex Supreme pad is composed of several layers, including a firm but resilient, 1 mm to 2 mm thick, porous bottom layer comprised of a polyester  
15 felt and polyurethane binder. A spongy and resilient microporous urethane layer of about 0.05 mm to 0.3 mm thickness is laminated onto the bottom layer. The top layer is comprised of vertical urethane structures having vertical, tapered pores,  
20 the taper of the pores narrowing toward the top of the pad. The top layer is very soft, porous and elastic. In a typical polishing operation, the top layer of such a stratified pad wears rapidly. As the top layer wears and subsequent layers are  
25 exposed, the polishing properties of the pad vary, resulting in non-uniform polishing rates and producing inconsistent polishing characteristics on the surface of the workpiece.

Conventional polishing pads typically  
30 have textured surfaces. The "microtexture" of a pad is the intrinsic microscopic bulk texture of the pad after manufacture. Some of the factors which influence the static morphology or

- 3 -

microscopic bulk texture of a conventional pad are the nature or texture of the work surface, such as waves, holes, creases, ridges, slits, depressions, protrusions and gaps, and the size, shape, and distribution, frequency or spacing of individual features or artifacts. In typical polishing pads, the microtexture of the pad is largely random and is the result of factors intrinsic to the manufacturing process. Because of the large number of variables in the manufacturing process, few attempts have been made to control variables such as pore size, shape and distribution. Other characteristics which may affect the pad texture are hardness, resilience, thickness, permeability, and resistivity, to name a few.

"Minitexturized" pads have intermediately sized textured artifacts on the pad, which may be produced by use of lasers or the incorporation of air or gas within the pad material.

"Macrotextures", or larger size textured artifacts, may be imposed on the work surface of a pad by embossing, skiving, perforating and/or machining, for example. In conventional polishing pads, the spacing and/or size of individual macrotexture artifacts or features is generally greater than 5 mm. The spacing and size of these artifacts are typically very regular and repetitive.

Conventional polishing pads may include various solid particulates, such as cerium oxide, titanium oxide, aluminum oxide, barium carbonate, glass dust and fibers, diatomaceous earth, rouge, calcium carbonate, diamond, and carbon, for

- 4 -

example. Typically, mechanical mixing and distribution of such particulates has been poorly controlled.

It would be desirable to have a substrate for polishing and other operations in which the particle distribution of additives may be optimized on a molecular scale. It is also desirable to have a polymeric substrate in which the surface of the substrate regenerates itself and does not vary appreciably as the surface is contacted with a workpiece. A polishing substrate which has a series of hardness variations on a micro scale and which can be texturized on a mini or macro scale to help remove dross (effluent, grindings, etc.) during polishing operations would also be advantageous.

#### Summary of the Invention

Briefly, one aspect of the present invention is an article of manufacture for altering a surface of a workpiece. The article comprises a polymeric matrix impregnated with a plurality of polymeric microelements. Each polymeric microelement has a void space therein. The article has a work surface and a subsurface proximate to the work surface. When the article is in contact with a working environment, the polymeric microelements at the work surface of the article are less rigid than polymeric microelements embedded in the subsurface.

A further aspect of the present invention is an article of manufacture for altering a surface of a workpiece. The article comprises a polymeric

- 5 -

matrix impregnated with a plurality of polymeric microelements. Each polymeric microelement has a void space therein. The article has a texturized work surface and a subsurface proximate to the work surface. When the article is in contact with the working environment, the polymeric microelements at the work surface of the article are less rigid than polymeric microelements embedded in the subsurface.

Another aspect of the present invention is a semiconductor device planarized by contact with an article. The article comprises a polymeric matrix impregnated with a plurality of polymeric microelements. Each polymeric microelement has a void space therein. The article has a work surface and a subsurface proximate to the work surface. When the article is in contact with the working environment, the polymeric microelements at the work surface of the article are less rigid than the polymeric microelements embedded in the subsurface. The semiconductor device includes a surface planarized by contact with the work surface of the article.

Another aspect of the present invention is a method for regenerating a work surface of an article in contact with a working environment. The article is for altering a surface of a workpiece. The method comprises the steps of: providing an article comprising a polymeric matrix; impregnating the polymeric matrix with a plurality of polymeric microelements, each polymeric microelement having a void space therein, wherein the article has a work surface and a subsurface proximate the work surface; and opening at least a portion of shells

- 6 -

of a portion of polymeric microelements located proximate to the work surface, such that the open polymeric microelements are less rigid than polymeric microelements embedded in the subsurface.

- 5 Yet another aspect of the present invention is a method for regenerating a work surface of an article. The article is for altering the surface of a workpiece. The method comprises the steps of: providing an article comprising a
- 10 polymeric matrix; impregnating the polymeric matrix with a plurality of polymeric microelements, each polymeric microelement having a void space therein, wherein the article has a work surface and a subsurface proximate to the work surface;
- 15 contacting said article with a working environment; and chemically altering at least a portion of shells of a portion of polymeric microelements located proximate the work surface, such that the chemically altered polymeric microelements are less
- 20 rigid than polymeric microelements embedded in the subsurface.

- Another aspect of the present invention is a method for decreasing the effective rigidity of polymeric microelements located at a portion of
- 25 a work surface of an article in contact with a working environment. The method comprises the steps of: providing an article comprising a polymeric matrix; impregnating the polymeric matrix with a plurality of polymeric microelements, each
- 30 polymeric microelement having a void space therein, wherein the article has a work surface and a



- 7 -

subsurface proximate to the work surface; and texturizing the portion of the work surface including said polymeric microelements.

A further aspect of the present invention is a method of planarizing a surface of a semiconductor device utilizing an article. The method comprises the steps of: providing an article comprising a polymeric matrix; impregnating the polymeric matrix with a plurality of polymeric microelements, each polymeric microelement having a void space therein, wherein the article has a work surface and a subsurface proximate to the work surface; contacting the article with a working environment such that polymeric microelements at the work surface of the article are less rigid than polymeric microelements located in the subsurface; and contacting the surface of the semiconductor device with a work surface of the article.

#### Brief Description of the Drawings

The foregoing summary, as well as the following detailed description of the preferred embodiments, will be better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there are shown in the drawings embodiments which are presently preferred, it being understood, however, that the invention is not limited to the specific methods and instrumentalities disclosed. In the drawings:

Fig. 1 is a schematic cross-sectional diagram of an article, in accordance with the present invention;

- 8 -

Fig. 2 is a schematic cross-sectional diagram of an alternative embodiment of an article according to the present invention;

Fig. 3 is a schematic cross-sectional diagram of an alternative embodiment of an article according to the present invention, in which microelements at the work surface of the article have swelled when in contact with the working environment;

Fig. 4 is a graph of planarization rate as a function of distance between features on the surface of a typical semiconductor device;

Fig. 5 is a schematic diagram of an alternative embodiment of a minitexturized pad according to the present invention;

Fig. 6 is an enlarged partial cross-sectional view of the pad of Fig. 5, taken along line 6-6;

Fig. 7 is a schematic diagram of an alternative embodiment of a macrotexturized pad according to the present invention;

Fig. 8 is an enlarged partial cross-sectional view of the pad of Fig. 7, taken along line 8-8;

Fig. 9 is a alternative embodiment of a fractal patterned minitexturized pad according to the present invention;

Fig. 10 is a bar graph showing specific gravity of an article according to the present invention as a function of the flow rate of microspheres; and

- 10 -

cerium oxide and garnet; bases; acids; salts; surfactants, and/or other agents depending upon the nature of the workpiece.

The article 10 et seq. is useful for  
5 altering a surface (not shown) of a workpiece (also not shown) by a polishing operation, such as lapping, planarizing, grinding or shaping, to name a few. The workpieces to be polished preferably comprise friable substances, such as quartz,  
10 silicon, glass, electronic and optical substrates, and high density multi-component electronic devices, for example. The workpiece may be a semiconductor device (not shown) having multiple layers of polysilicone, thermal oxides, and  
15 metallic materials, each layer of which may be planarized before a subsequent layer is deposited thereon.

As best shown in Fig. 1, the article 10 comprises a polymeric matrix 14 which is preferably  
20 impervious to aqueous fluid slurries typically used in polishing and planarization operations. The polymeric matrix 14 may be formed from urethanes, melamines, polyesters, polysulfones, polyvinyl acetates, fluorinated hydrocarbons, and the like,  
25 and mixtures, copolymers and grafts thereof. One of ordinary skill in the art would understand that any other polymer having sufficient toughness and rigidity to resist abrasive wear during polishing operations may be used, in keeping with the spirit  
30 and scope of the present invention. As presently preferred, the polymeric matrix 14 comprises a urethane polymer. The urethane polymer is preferably formed from a polyether-based liquid urethane, such as the Adiprene line of products

- 10 -

cerium oxide and garnet; bases; acids; salts; surfactants, and/or other agents depending upon the nature of the workpiece.

The article 10 et seq. is useful for  
5 altering a surface (not shown) of a workpiece (also not shown) by a polishing operation, such as lapping, planarizing, grinding or shaping, to name a few. The workpieces to be polished preferably comprise friable substances, such as quartz,  
10 silicon, glass, electronic and optical substrates, and high density multi-component electronic devices, for example. The workpiece may be a semiconductor device (not shown) having multiple layers of polysilicone, thermal oxides, and  
15 metallic materials, each layer of which may be planarized before a subsequent layer is deposited thereon.

As best shown in Fig. 1, the article 10 comprises a polymeric matrix 14 which is preferably  
20 impervious to aqueous fluid slurries typically used in polishing and planarization operations. The polymeric matrix 14 may be formed from urethanes, melamines, polyesters, polysulfones, polyvinyl acetates, fluorinated hydrocarbons, and the like,  
25 and mixtures, copolymers and grafts thereof. One of ordinary skill in the art would understand that any other polymer having sufficient toughness and rigidity to resist abrasive wear during polishing operations may be used, in keeping with the spirit  
30 and scope of the present invention. As presently preferred, the polymeric matrix 14 comprises a urethane polymer. The urethane polymer is preferably formed from a polyether-based liquid urethane, such as the Adiprene line of products

- 11 -

which are commercially available from Uniroyal Chemical Co., Inc. of Middlebury, Connecticut. The preferred liquid urethane contains about 9 to about 9.3% by weight free isocyanate. Other isocyanate bearing products and prepolymers may also be used in keeping with the spirit and scope of the present invention.

The liquid urethane is preferably one which reacts with a polyfunctional amine, diamine, triamine or polyfunctional hydroxyl compound or mixed functionality compounds such as hydroxyl/amines dwelling in urethane/urea crosslinked networks to permit the formation of urea links and a cured/crosslinked polymer network. As presently preferred, the liquid urethane is reacted with 4,4'-methylene-bis [2-chloroaniline] ("MOCA"), which is commercially available as the product Curene® 442, from Anderson Development Co. of Adrian, Michigan.

As best shown in Fig. 1, the polymer matrix 14 is impregnated with a plurality of polymeric microelements 16. Preferably, at least a portion of the polymeric microelements are generally flexible. Suitable polymeric microelements include inorganic salts, sugars and water-soluble gums and resins. Examples of such polymeric microelements include polyvinyl alcohols, pectin, polyvinyl pyrrolidone, hydroxyethylcellulose, methylcellulose, hydropropylmethylcellulose, carboxymethylcellulose, hydroxypropylcellulose, polyacrylic acids, polyacrylamides, polyethylene glycols, polyhydroxyetheracrylates, starches, maleic acid copolymers, polyethylene oxide,

- 12 -

polyurethanes and combinations thereof. The microelements 16 may be chemically modified to change the solubility, swelling and other properties by branching, blocking, and crosslinking, for example.

As presently preferred, each of the polymeric microelements 16 has a mean diameter which is less than about 150  $\mu\text{m}$ , and more preferably a mean diameter of about 10  $\mu\text{m}$ . One of ordinary skill in the art would understand that the mean diameter of the microelements may be varied and that microelements 16 of the same or different sizes or mixtures of different microelements 16 may be impregnated in the polymeric matrix 14, as desired.

As presently preferred, each of the polymeric microelements 16 are spaced apart about 1  $\mu\text{m}$  to about 100  $\mu\text{m}$ . Preferably, the polymeric microelements 16 are substantially uniformly distributed throughout the polymeric matrix 14 by high shear mixing. The resulting composite mixture is transferred to a conventional mold before the viscosity of the reacted urethane polymer becomes too great to permit sufficient blending of the microelements with the polymer mixture. One of ordinary skill in the art would understand that the low viscosity window may vary at different temperatures for different thermosetting plastics and curing agents. The resulting mixture is gelled in the mold for about 15 minutes. The gelling time may vary based upon factors such as temperature and selection of the polymer matrix and microelements. The composite is then cured at about 200-225°F for

- 13 -

about 4-6 hours and cooled to room temperature (about 70°F). The curing temperature may vary depending upon the polymer matrix and type of microelements used, among other factors.

5           The resulting article 10 is removed from the mold and cut, sliced, etc. to the desired thickness and shaped to form polishing pads 12. One of ordinary skill in the art would understand that the molded composite may be sliced, cut or  
10 otherwise machined to any thickness or shape as desired, in accordance with the present invention.

          Depending upon the intended application or operation, at least a portion of the polymeric microelements 16 may be generally spherical in  
15 shape, as shown in Fig. 1. Preferably such microspheres are hollow, each microsphere having a shell with a thickness of about 0.1  $\mu$ m.

          As best shown in Fig. 1, each polymeric microelement 16 has a void space 22 therein. At  
20 least some of the polymeric microelements 16 preferably have a plurality of void spaces 22 therein, as best shown in Fig. 3. It is preferred (but not required) that each void space 22 generally contains a gas at a pressure greater than  
25 atmospheric pressure to help maintain the structural integrity of the microelements 16', 16, respectively, both at the work surface 18 and subsurface 24 of the polymeric matrix 14.

          The polymeric microelements may have  
30 permeable or puncturable shells 20, best shown in Fig. 11, so that the void spaces 22 within the microelements 16' may be rendered open to the working environment.

- 14 -

As best shown in Fig. 1, in a preferred embodiment of the present invention, at least a portion of the polymeric microelements 16' located at the work surface 18 soften upon contact with the working environment (not shown) or polishing slurry. For example, water soluble cellulose ethers such as methylcellulose will dissolve upon contact with water in an aqueous polishing slurry.

As best shown in Fig. 1, in another preferred embodiment, at least a portion of the polymeric microelements 16' located at the work surface 18 swell upon contact with the working environment. For example, longer chain cellulose ethers may swell upon contact with water in an aqueous polishing slurry.

The article 10 has a work surface 18 and a subsurface 24 proximate to the work surface 18, as best shown in Figs. 1-3. Preferably, the work surface 18 is about 5  $\mu\text{m}$  to about 60  $\mu\text{m}$  thick. The thickness of the article 10 is preferably between about 300  $\mu\text{m}$  and about 400  $\mu\text{m}$  in a direction generally perpendicular to a major plane (not shown) of the work surface 18.

An advantage of the present invention is that polymeric microelements 16' at the work surface 18 of the article 10 are less rigid than the polymeric microelements 16 embedded in the subsurface 24 when the article 10 is in contact with the working environment. Also, the less rigid polymeric microelements 16' provide less support for the portion 15 of the polymeric matrix 14 which surrounds the less rigid microelements, thereby reducing the effective rigidity of that surrounding



- 15 -

portion 15 of the polymeric matrix. Therefore, at least two levels of hardness are created in the article 10, the work surface 18 being generally softer than the subsurface 24.

5 Another advantage of the present invention is that as the work surface 18 of the article wears, such as by contact with the surface of a workpiece or the working environment, the subsurface 24 immediately adjacent to the work  
10 surface 18 becomes the new work surface and the two levels of hardness are regenerated continuously, which permits more even and consistent polishing of the workpiece and more even wear of the pad 12.

Different aspects of the present  
15 invention will now be described and explained further by reference to the following specific, illustrative, non-limiting examples.

#### EXAMPLE 1

A polymeric matrix was prepared by mixing  
20 2997 grams of Uniroyal Adiprene L-325 polyether-based liquid urethane with 768 grams of Curene® 442 (4,4'-methylene-bis [2-chloroaniline] ("MOCA") at about 150°F. At this temperature, the urethane/polyfunctional amine mixture has a pot  
25 life of about 2.5 minutes (the "low viscosity window").

During this low viscosity window, 69 grams of Expancel 551 DE hollow polymeric microspheres were blended with the polymer mixture  
30 at 3450 rpm using Rodel Incorporated high shear blending and mixing equipment to generally evenly distribute the microspheres in the polymer mixture.

- 16 -

The mixture was transferred to a conventional mold during the low viscosity window and permitted to gel for about 15 minutes.

The mold was next placed in a curing  
5 oven, such as is commercially available from Koch Oven Corporation. The mixture was cured in the oven for about 5 hours at about 200°F. The power to the oven was then shut off and the mixture permitted to cool in the oven for about 4-6 hours until the  
10 temperature of the molded article 10 was about 70°F (room temperature). The molded article was then cut to form polishing pads. The mean distance between the microspheres in the resulting polishing pad 12 is believed to be between about 75 and about  
15 300  $\mu\text{m}$ .

As shown in Fig. 4, the planarization rate ( $\mu\text{m}^{-1}$ ) is more than four times greater for a 20 mil thick urethane pad having Expancel microspheres embedded therein (as designated by the  
20 squares) than a similar urethane pad without microspheres (as designated by the circles) when the pads were used to planarize a typical semiconductor device having features or chips spaced about 1 mm apart. In other words, Fig. 4  
25 shows that a device may be planarized about four times faster by using a urethane pad having microelements embedded therein than without microelements, according to the present invention.

As shown in Fig. 10, the specific gravity  
30 of the molded article decreases as the flow rate of microspheres is increased. Generally, it is preferred that the specific gravity of the pad be

- 17 -

about 0.75 to about 0.8, which corresponds to an Expancel microsphere flow rate of about 53 grams/minute.

#### EXAMPLE 2

5           A polymeric matrix was prepared by mixing  
2997 grams of Uniroyal Adiprene L-325 urethane with  
768 grams of Curene™ 442 MOCA and high shear mixing  
the urethane polymer with 87 grams of powdered  
10   partially acetylated polyvinyl alcohol, which is  
commercially available from Air Products and  
Chemicals Corporation of Allentown, Pennsylvania.  
During the low viscosity window (2.5 mins.), the  
mixture was poured into a mold, gelled, cured in an  
oven for about six hours at about 225°F and cooled  
15   to room temperature in a similar manner to that of  
the article of Example 1. It is believed that  
essentially no reaction of the OH groups of the  
polyvinyl alcohol and the isocyanate group of the  
liquid urethane occurs because of the much faster  
20   reaction of the urethane with the MOCA amino  
groups.

#### EXAMPLE 3

          A polymeric matrix was prepared in a  
manner similar to that of Example 1 by mixing 3625  
25   grams of Adiprene L-213 to 930 grams Curene™ 442  
MOCA. During the low viscosity window (about 2.5  
mins.), 58 grams of pectin powder, which is  
commercially available from Freeman Industries,  
Inc. of Tuckahoe, New York, was high shear mixed  
30   with the urethane polymer to evenly distribute the  
pectin powder throughout the urethane mixture.

- 18 -

During the low viscosity window (2.5 mins.), the resulting urethane/pectin mixture was poured into a mold, gelled and cured for about six hours at 225°F and cooled and processed in a manner similar to  
5 that set forth in Example 1.

#### EXAMPLE 4

A polymer matrix was prepared by mixing 2997 grams of Adiprene L-325 with 65 grams of polyvinyl pyrrolidone powder, which is commercially  
10 available from BASF Chemicals Corp. of Parsippany, New Jersey or GAF Chemicals Corp. of Wayne, New Jersey, for about 30 seconds to form a homogenous blend. Curene™ 442 MOCA (768 grams) was melted at a temperature of about 212-228°F and high shear  
15 blended with the urethane/polyvinyl pyrrolidone mixture and poured into a mold during the low viscosity window, namely before about 2.5 minutes had elapsed. The resulting mixture was gelled, heated for about six hours at about 225°F, cooled,  
20 and cut into polishing pads in a manner similar to that set forth in Example 1.

#### EXAMPLE 5

A polymeric matrix was prepared by mixing 3625 grams of Adiprene L-213 with 930 grams of  
25 Curene™ 442 MOCA. During the low viscosity window, 65 grams of white, free-flowing hydroxyethylcellulose (commercially available from Union Carbide Chemicals and Plastics Corp. of Danbury, Connecticut) was blended with the urethane mixture.  
30 The hydroxyethylcellulose is insoluble in organic

- 19 -

solvents but dissolves in hot or cold water. The composite blend was then processed in a manner similar to that set forth in Example 1.

In alternative embodiments best shown in Figs. 5-9, the work surface 18 of the article 10 may further include a mini or macro pattern or texture 26 which includes recessed and/or elevated portions or artifacts 28. The texture 26 may be formed upon at least a portion of the work surface 18 by mechanical texturizing methods, such as machining, embossing, turning, grinding, replicating and lasering the work surface 18. One of ordinary skill in the art would understand that the texture 26 may be formed by a variety of other mechanical work or chemical methods, such as etching, for example.

By texturizing the work surface 18, up to 50% or more surface area may be exposed to facilitate removal of dross during polishing. In addition, texturing of the work surface 18 enhances the polishing action by exposing a greater number of microelements 16' to the working environment. The texture 26 may be formed in a variety of patterns, contours, grooves, spirals, radials, dots, or any other shape as desired. Texturing the work surface 18 of the pad 12 offers a series of hardness variations on the microscale. For example, the artifacts 28 may be shaped to form cones or blades having a harder core and a softer outer surface in addition to the harder subsurface 24.

- 20 -

Preferably, the artifacts 28 are spaced apart between about 0.1 mm to about 10 mm and have a depth between about 1 mm and about 10 mm.

Generally, it is preferred that the artifacts 28 have a length in a first dimension less than about 1000 times a mean diameter of a polymeric microelement 16. It is also preferred that the artifacts 28 have a depth less about 2000 times a mean diameter of a polymicroelement 16.

As best shown in Figs. 5 and 6, the work surface 18 may include a minitexture including artifacts 28 having a width between about 1000 um and 5 mm. The minitexture shown in Figs. 5 and 6 is a concentric circular pattern, although one of ordinary skill in the art would understand that the minitexture may be a spiral or other pattern, including those discussed above.

As best shown in Figs. 7 and 8, the work surface 18 may include a macrotexture including artifacts 28, each artifact 28 having a width greater than about 5 mm. As shown in Figs. 7 and 8, the minitexture is a generally square grid, although one of ordinary skill in the art would understand that the minitexture may be formed in any pattern, including those discussed above, as desired.

The macrotexture and minitexture may be formed by typical machining methods, such as embossing, turning, grinding, replicating and lasering and a variety of other methods well known to those of ordinary skill in the art.

- 21 -

EXAMPLE 6

Using a standard lathe and a single point tool, the work surfaces 18 shown in Figs. 5-8 were cut by superimposing circular and square grid patterns, respectively, on the work surface 18 which was vacuum mounted to the lathe or milling machine's rotating plate. A conventional horizontal milling machine with ganged cutting tools or custom cutting combs with regularly spaced serrated teeth was used to machine the work surface 18 in the desired pattern.

As best shown in Fig. 5, the annular minitexture was machined into the polishing pad to form grooves having 1.397 mm (0.055") pitch, each with a depth of 0.356 mm (0.014"). The groove form is buttress thread with a 60 degree ramp towards the pad's inside diameter, as shown in Fig. 6.

The square grid macrotexture 28 shown in Figs. 7 and 8 was machined on a horizontal milling machine to produce squares having grooves 0.813 mm (0.032") wide and 0.635 mm (0.025") deep defining 6.35 mm (0.025") artifacts 28.

As best shown in Fig. 9, the work surface 18 may also include a minitexture including artifacts 28 having a width between about 1000 um and 5 mm produced by use of a carbon dioxide laser. Preferably, the microtexture is produced in the shape of a fractal pattern on the work surface 18. As herein defined "fractal pattern" means a repeating pattern which has repeating artifacts in which the artifacts are different from each other. The fractal pattern may be generated by deterministic or non-deterministic mathematical

- 22 -

formulas, such as the Gosper Island variant of the Koch Island & Lake fractal pattern ("Gosper pattern") (shown in Fig. 9). Suitable fractal models include the round, spherical and swiss-  
5 cheese tremas, although one of ordinary skill in the art would understand that other suitable fractal patterns may be used in accordance with the present invention, as desired. Preferably, the fractal pattern is chaotic or random.

10

EXAMPLE 7

As best shown in Fig. 9, grooves or minitextures were machined into a polishing pad 12 using a typical carbon dioxide laser with a continuous wave output of 100 watts. The power  
15 rating, output and beam focus were selected to cut a groove with a depth of about 0.458 mm (0.018") and having a width of less than about 0.127 mm (0.005"). The minitexture was the Gosper Island variation of the Koch Island & Lake fractal pattern  
20 discussed above. The fractal pattern image was read and programmed electronically into a conventional computer numerical controller, which controlled movement of the laser beam to form the fractal pattern on the work surface 18 of the pad  
25 12. An adhesive mask was used to eliminate vapor trails from accumulating on the pad. The adhesive mask also reduced the attendant minor fusing on the edges of the grooves.

Alternatively, or additionally, isolated  
30 "mesa" patterns may be embossed onto the work surface 18 to form a minitexture. For example, a conventional 30 ton press machine may be used to



- 23 -

apply about 25 tons of pressure to emboss a minitexture onto the work surface 18 of a pad 12. Heat may be applied to enhance the embossing effect.

5           The method according to the present invention of planarizing a surface of a semiconductor device utilizing an article 10 et seq. according to the present invention will now be described generally.

10           With reference to Figs. 1-3, the method generally comprises the initial step of providing an article 10 or 110 comprising a polymeric matrix 14. The polymeric matrix 14 is impregnated with a plurality of polymeric microelements 16. The  
15 details of providing the polymeric matrix 14 and impregnating the matrix 14 with the microelements 16 are discussed above and further discussion thereof is not believed to be necessary nor is it limiting. Preferably, the work surface 18 of the  
20 article 10 or 110 is textured to form artifacts 28 to provide an enlarged work surface area and expose microelements 16 to the working environment which would not normally be exposed if the work surface 18 were generally flat.

25           The method further comprises the step of contacting at least a portion of the work surface 18 of the article 10 or 110 with the working environment such that the polymeric microelements 16' at the work surface 18 of the article 10 or 110  
30 are less rigid than the polymeric microelements 16 located in the adjacent subsurface 24. For example, a portion of a shell 20 of at least a portion of the polymeric microelements 16 located

- 24 -

proximate the work surface 18 may be opened by at least one of skiving, abrading, cutting and puncturing a portion of the shell 20 or by chemically altering or softening a portion of the shell 20 to render a portion of the polymeric microelements 16' of the work surface 18 less rigid than the microelements 16 located in the subsurface 24. Details as to how the polymeric microelements 16' at the work surface 18 may be made less rigid are discussed above and further discussion thereof is not believed to be necessary nor limiting.

The method further comprises the step of contacting the surface (not shown) of the semiconductor device (also not shown) with at least a portion of the work surface 18 of the article such that the surface of the semiconductor device is sufficiently planarized. The article 10 or polishing pad 12 may be attached to a conventional polishing machine such as are well known to those of ordinary skill in the art. Preferably, the work surface 18 is oriented generally parallel to the surface of the semiconductor device to be planarized and may be moved in linear or circular sliding contact, for example, to planarize or abrade the surface of the semiconductor device, as desired.

As the work surface 18 of the pad 12 is abraded by sliding contact with the surface of the semiconductor device, portions of the subsurface 24 are exposed and microelements 16 in the subsurface 24 are abraded or chemically altered or softened to form a new work surface 18 having similar physical properties to the previously abraded work surface.

- 25 -

Therefore, the work surface 18 in contact with the surface of the semiconductor device is essentially continuously regenerated to provide a consistent planarizing or polishing action upon the surface of the semiconductor device.

A method according to the present invention of regenerating the work surface 18 of an article according to the present invention will now be described generally.

Referring now to Fig. 11, the method generally comprises the initial steps of providing an article 410 or pad 12 comprising a polymeric matrix 14 and impregnating the matrix 14 with a plurality of polymeric microelements 16. The details of forming the article 10 are discussed at length above and further discussion thereof is not believed to be necessary nor limiting.

The method further comprises the step of opening at least a portion of a shell 20 of at least a portion of the polymeric microelements 16 located proximate to the work surface 18 such that the open microelements 16' are less rigid than the microelements 16 in the subsurface 24. The step of opening the polymeric microelements may include at least one of skiving, abrading, cutting and puncturing a portion of each of the shells 20 of the microelements 16. As best shown in Fig. 11, the shells 20 of the microelements 16' at the work surface 18 may be punctured by a combined pommelgation and perforation device 30, a portion of which is shown in cross-section in Fig. 11. The device 30 may be formed from any material having sufficient rigidity to puncture the work surface 18

- 26 -

and microelements 16, such as stainless steel, aluminum and other metals, for example. The device 30 includes a plurality of sharp implements or needles 32 for puncturing at least a portion of a  
5 shells 20 of polymeric microelements 16 located proximate the work surface 18.

In addition to the needles 32, the device 30 includes at least one, and preferably a plurality of pads 34 for preventing the needles 23  
10 from puncturing the work surface 18 too deeply. Preferably, the needles 32 puncture the work surface 18 to a depth of about 60  $\mu\text{m}$ , although one of ordinary skill in the art would understand that the puncturing depth of the device 30 may any depth  
15 greater or less than 60  $\mu\text{m}$ , as desired. For example, longer needles 32 could be used to puncture the work surface 18 to a depth greater than 60  $\mu\text{m}$ .

One of ordinary skill in the art would  
20 understand that the microelements 16 may be opened or the pad 12 may be punctured one or more times, as needed.

In an alternative embodiment, at least a portion of the shells 20 of polymeric microelements  
25 16 located proximate the work surface 18 may be chemically altered or softened by the work environment such that the partially altered polymeric microelements 16 at the work surface 18 are less rigid than the polymeric microelements 16  
30 embedded in the subsurface 24. For example, the polymeric microelements 16 may be formed from water soluble cellulose ethers comprising methylcellulose

- 27 -

or hydroxypropylmethylcellulose which at least partially dissolve when contacted with a working environment comprising water.

From the foregoing description, it can be  
5 seen that the present invention comprises articles of manufacture for altering a surface of a workpiece, such as a semiconductor device, and methods for decreasing the effective rigidity of a polymeric microelement located at a portion of a  
10 work surface of such an article, regenerating the work surface of such an article, and planarizing a surface of a semiconductor device utilizing such an article. The present articles may be used to more rapidly and evenly polish or planarize a substrate  
15 or other workpiece.

It will be appreciated by those skilled in the art that other changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It should be  
20 understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover all modifications which are within the spirit and scope of the invention, as defined by the appended claims.

- 28 -

CLAIMS

1. An article of manufacture for altering a surface of a workpiece, said article comprising a polymeric matrix impregnated with a plurality of polymeric microelements, each polymeric microelement having a void space therein, said article having a work surface and a subsurface proximate to said work surface, wherein when said article is in contact with a working environment the polymeric microelements at said work surface of said article are less rigid than polymeric microelements embedded in said subsurface.

2. An article according to claim 1, wherein at least a portion of said polymeric microelements are generally flexible.

3. An article according to claim 1, wherein said polymeric microelements are substantially uniformly distributed throughout said polymeric matrix.

4. An article according to claim 1, wherein said polymeric matrix comprises a urethane polymer.

5. An article according to claim 1, wherein at least a portion of said polymeric microelements located at said work surface soften upon contact with said working environment.

6. An article according to claim 1, wherein at least a portion of said polymeric microelements located at said work surface swell upon contact with said working environment.

- 29 -

7. An article according to claim 1, wherein at least some of said polymeric microelements have a plurality of void spaces therein.

5           8. An article according to claim 1, wherein said void space contains a gas at a pressure greater than atmospheric pressure.

          9. An article according to claim 1, wherein each of said polymeric microelements has a  
10 mean diameter less than about 150  $\mu\text{m}$ .

          10. An article according to claim 9, wherein said mean diameter of each of said polymeric microelements is about 10  $\mu\text{m}$ .

          11. An article according to claim 1,  
15 wherein said polymeric microelements are spaced apart by about 1  $\mu\text{m}$  to about 100  $\mu\text{m}$ .

          12. An article according to claim 1, wherein at least a portion of said polymeric microelements are generally spherical in shape.

20           13. An article according to claim 1, wherein at least some of said polymeric microelements are hollow microspheres, each microsphere having a shell thickness of about 0.1  $\mu\text{m}$ .

25           14. An article according to claim 1, wherein at least a portion of said polymeric microelements have permeable shells so that said void space may be rendered open to said working environment.

30           15. An article according to claim 1, wherein said polymeric microelements comprise at least one material selected from the group consisting of polyvinyl alcohols, pectin, polyvinyl

- 30 -

pyrrolidone, hydroxyethylcellulose,  
methylcellulose, hydropropylmethylcellulose,  
carboxymethylcellulose, hydroxypropylcellulose,  
polyacrylic acids, polyacrylamides, polyethylene  
5 glycols, polyhydroxyetheracrylates, starches,  
maleic acid copolymers, polyethylene oxide, and  
polyurethanes.

16. An article according to claim 1,  
wherein the thickness of said work surface is about  
10 5  $\mu\text{m}$  to about 60  $\mu\text{m}$ .

17. An article according to claim 1,  
wherein the thickness of said article is between  
about 300  $\mu\text{m}$  and about 400  $\mu\text{m}$  in a direction  
generally perpendicular to a major plane of said  
15 work surface.

18. An article according to claim 1,  
wherein said work surface further comprises a  
microtexture including an artifact having a width  
less than about 1000  $\mu\text{m}$ .

20 19. An article according to claim 1,  
wherein said work surface further comprises a  
minitexture including an artifact having a width  
between about 1000  $\mu\text{m}$  and about 5 mm.

20. An article according to claim 1,  
25 wherein said work surface further comprises a  
macrotexture including an artifact having a width  
greater than about 5 mm.

21. An article according to claim 1,  
wherein said work surface further comprises a  
30 texture including a plurality of artifacts, each of  
said artifacts being spaced apart between about 0.1  
mm to about 10 mm and having a depth of between  
about 1 mm and about 10 mm.



- 31 -

22. An article according to claim 1,  
wherein said work surface further comprises a  
texture including an artifact having a length in a  
first dimension less than about 1000 times a mean  
5 diameter of said polymeric microelements.

23. An article according to claim 1,  
wherein said work surface further comprises a  
texture including an artifact having a depth less  
than about 2000 times a mean diameter of said  
10 polymeric microelements.

24. An article of manufacture for  
altering a surface of a workpiece comprising a  
polymeric matrix impregnated with a plurality of  
polymeric microelements, each polymeric  
15 microelement having a void space therein, said  
article having a texturized work surface including  
an artifact and a subsurface proximate to said work  
surface, wherein when said article is in contact  
with a working environment the polymeric  
20 microelements at said work surface of said article  
are less rigid than polymeric microelements  
embedded in said subsurface.

25. A semiconductor device planarized by  
contact with an article, said article comprising a  
25 polymeric matrix impregnated with a plurality of  
polymeric microelements, each polymeric  
microelement having a void space therein, said  
article having a work surface and a subsurface  
proximate to said work surface, wherein when said  
30 article is in contact with a working environment  
the polymeric microelements at said work surface of  
said article are less rigid than polymeric  
microelements embedded in said subsurface, whereby

- 32 -

said semiconductor device includes a surface planarized by contact with said work surface of said article.

26. A method for regenerating a work surface of an article in contact with a working environment, said article being for altering a surface of a workpiece, comprising the steps of:

providing an article comprising a polymeric matrix;

impregnating said polymeric matrix with a plurality of polymeric microelements, each polymeric microelement having a void space therein, wherein said article has a work surface and a subsurface proximate to said work surface; and

opening at least a portion of a shell of polymeric microelements located proximate said work surface, such that said open polymeric microelements are less rigid than polymeric microelements embedded in said subsurface.

27. A method according to claim 26, wherein the step of opening said shell of said polymeric microelements further comprises at least one of skiving, abrading, cutting and puncturing a portion of said shell of said microelements.

28. A method for regenerating a work surface of an article, said article being for altering a surface of a workpiece, comprising the steps of:

providing an article comprising a polymeric matrix;

- 33 -

impregnating said polymeric matrix with a plurality of polymeric microelements, each polymeric microelement having a void space therein, wherein said article has a work surface and a

5 subsurface proximate said work surface;

contacting said article with a working environment; and

chemically altering at least a portion of a shell of polymeric microelements located

10 proximate said work surface such that said partially altered polymeric microelements are less rigid than polymeric microelements embedded in said subsurface.

29. A method for decreasing the  
15 effective rigidity of polymeric microelements located at a portion of a work surface of an article in contact with a working environment, comprising the steps of:

providing an article comprising a  
20 polymeric matrix;

impregnating said polymeric matrix with a plurality of polymeric microelements, each polymeric microelement having a void space therein, wherein said article has a work surface and a  
25 subsurface proximate said work surface; and

texturizing said portion of said work surface including said polymeric microelements.

30. A method according to claim 29,  
including the step of microtexturizing said  
30 portion of said work surface.

31. A method according to claim 29,  
including the step of minitexturizing said portion of said work surface.

- 34 -

32. A method according to claim 29,  
including the step of macrotexturizing said portion  
of said work surface.

33. A method according to claim 29,  
5 wherein the step of texturizing said portion of  
said work surface further comprises at least one of  
machining, embossing, turning, grinding,  
replicating and lasering said portion of said work  
surface.

10 34. A method according to claim 29,  
including the step of fractal patterning said  
portion of said work surface.

35. A method according to claim 29,  
including the step of chaotically fractal  
15 patterning said portion of said work surface.

36. A method of planarizing a surface of  
a semiconductor device utilizing an article,  
comprising the steps of:

providing an article comprising a  
20 polymeric matrix;

impregnating said polymeric matrix with a  
plurality of polymeric microelements, each  
polymeric microelement having a void space therein,  
wherein said article has a work surface and a  
25 subsurface proximate said work surface;

contacting said article with a working  
environment such that polymeric microelements at  
said work surface of said article are less rigid  
than polymeric microelements located in said  
30 subsurface; and

contacting said surface of said  
semiconductor device with said work surface of said  
article.

1/6

FIG. 1

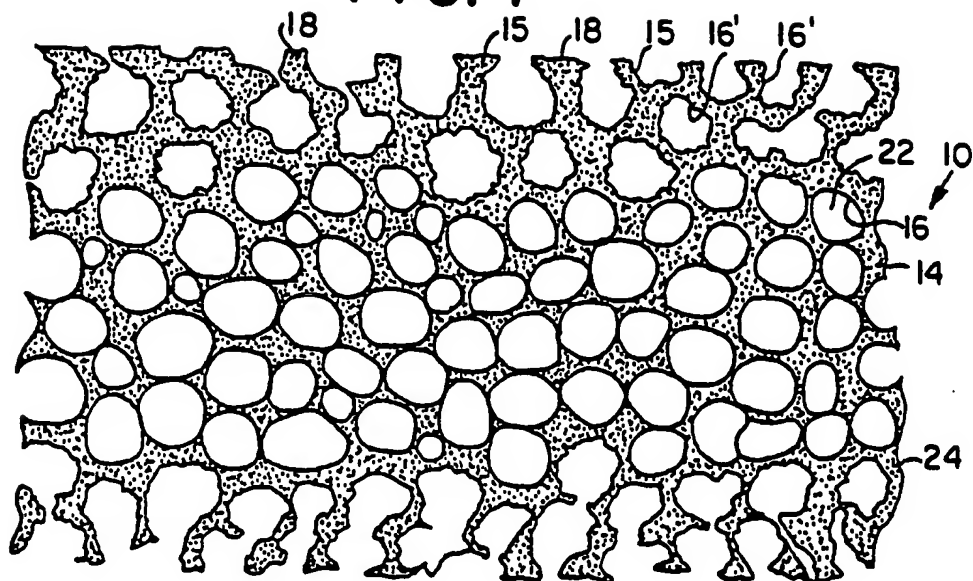
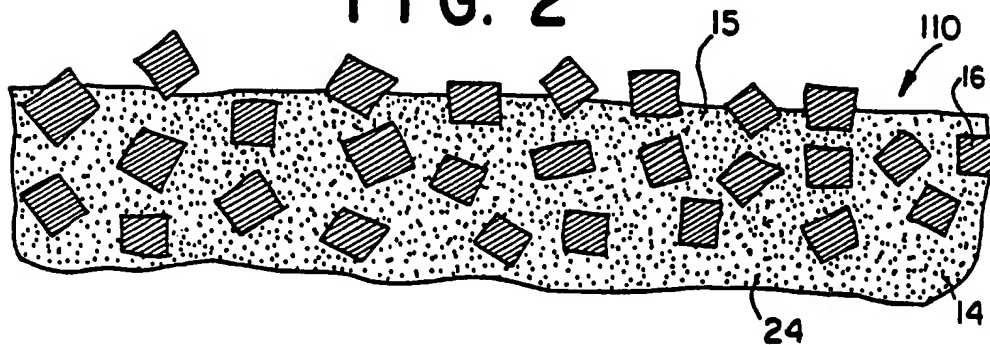


FIG. 2



2/6

FIG. 3

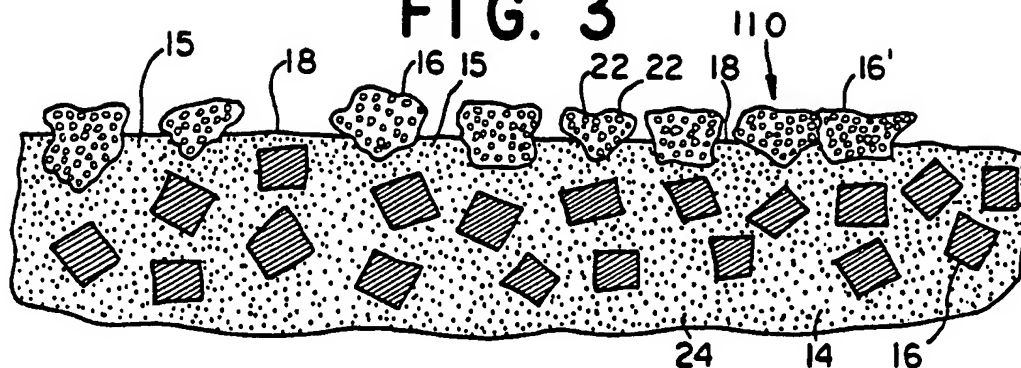
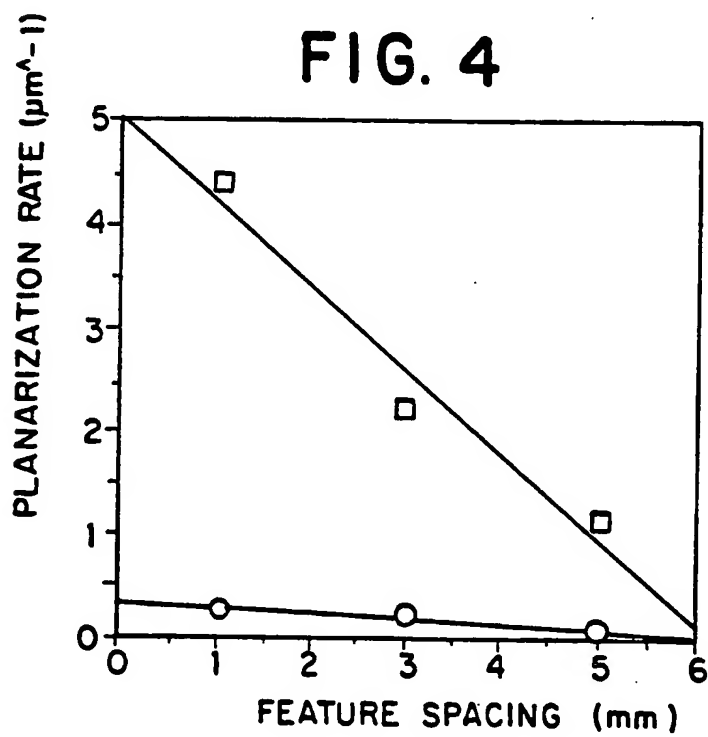


FIG. 4



3/6

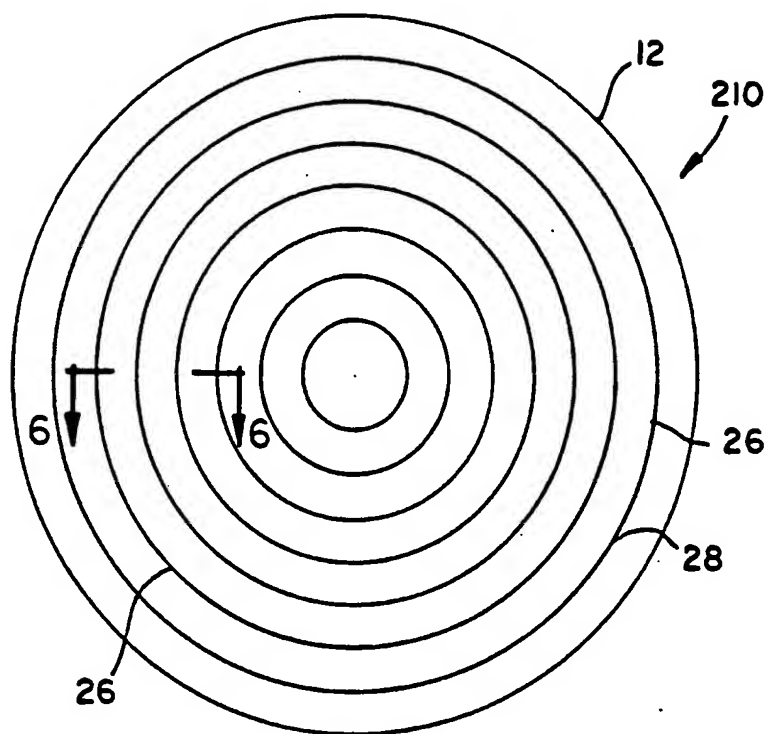


FIG. 5

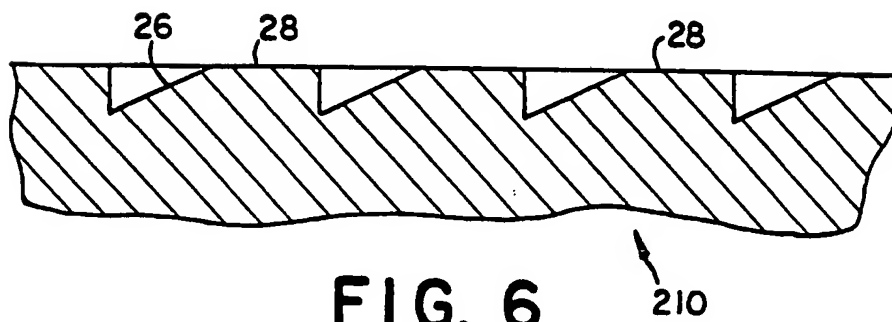


FIG. 6

4/6

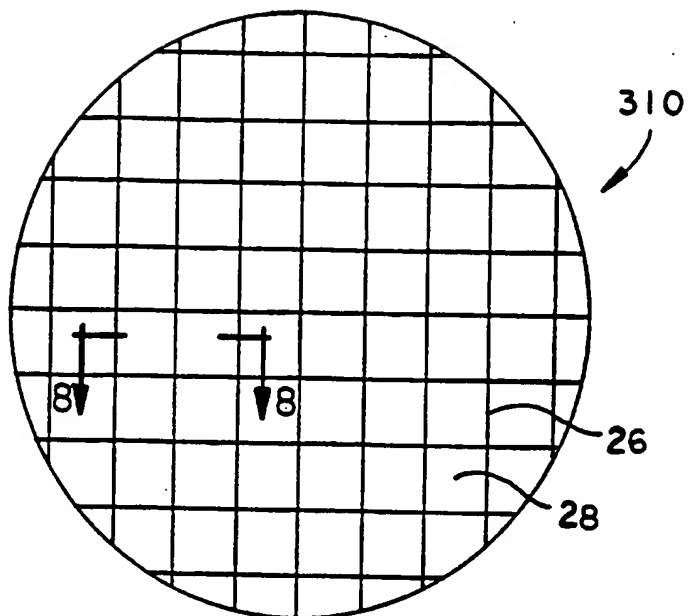


FIG. 7

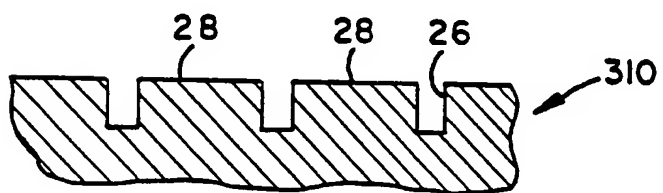


FIG. 8

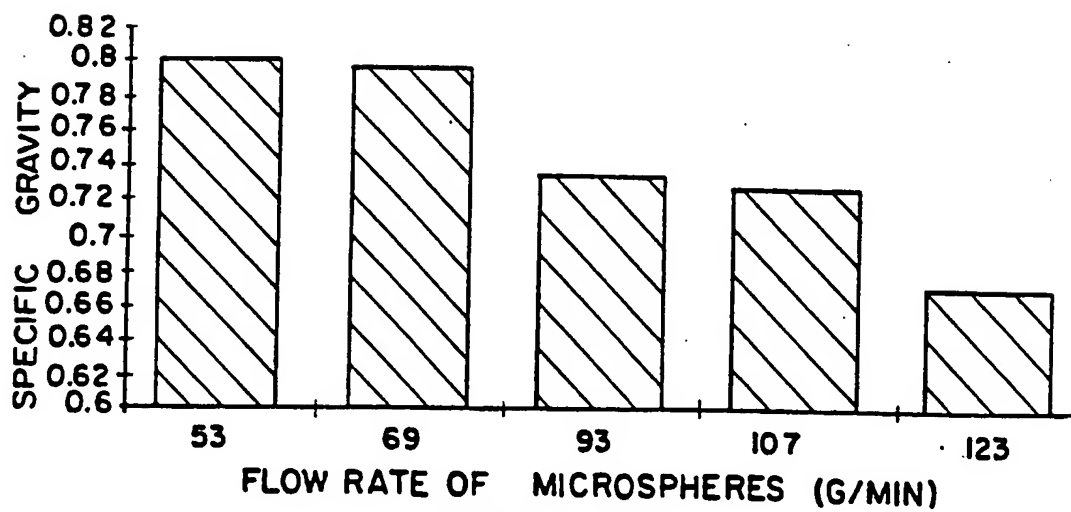
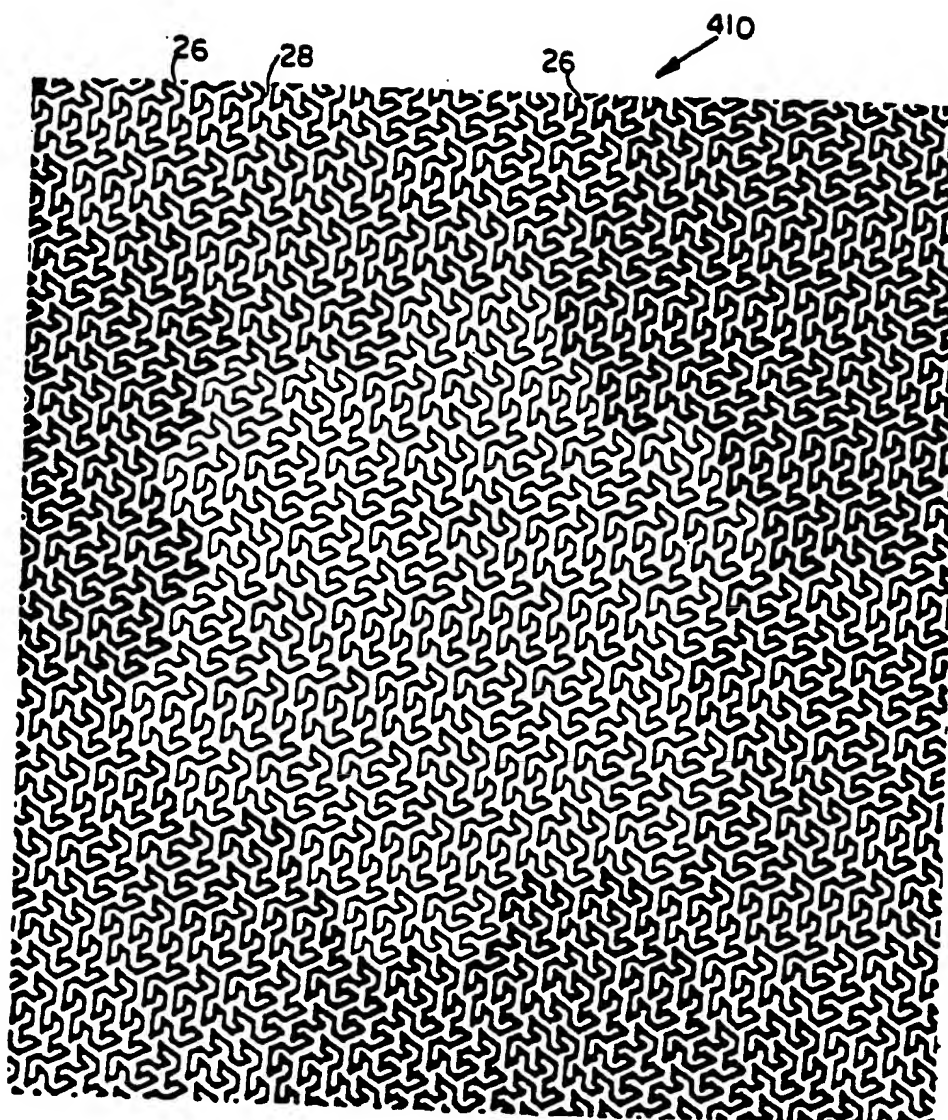


FIG. 10



5/6

FIG. 9



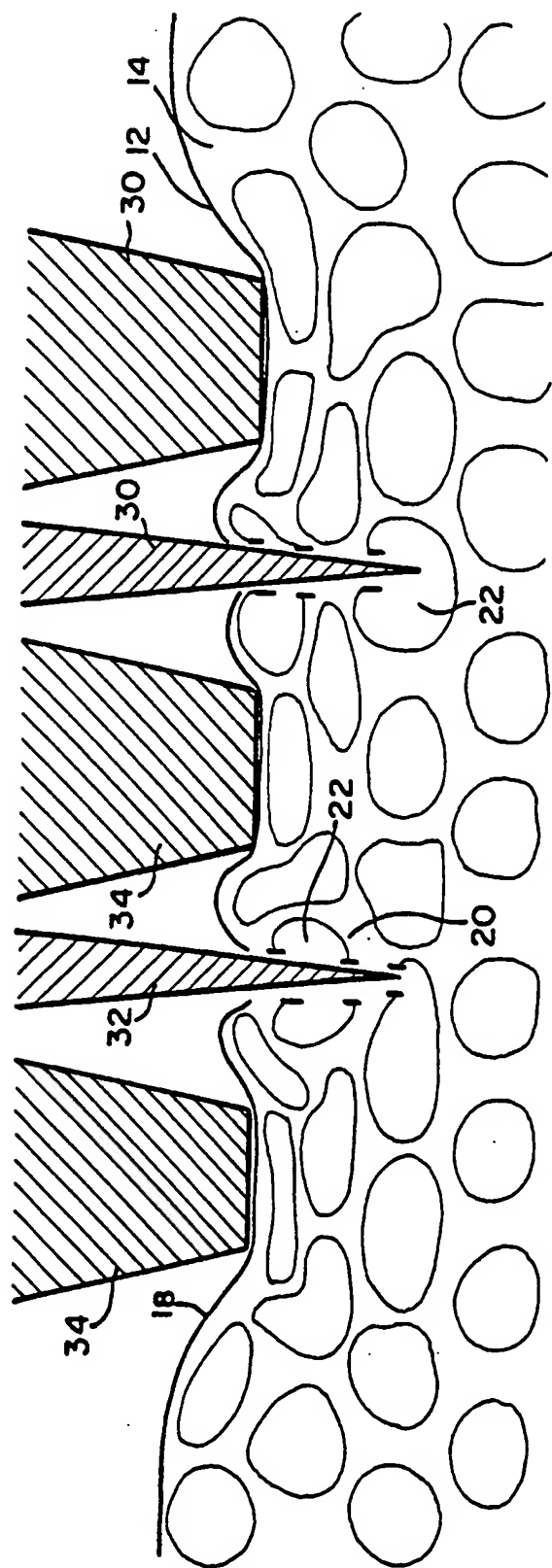


FIG. 11

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/07256

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/141, 143, 147, 323, 327; 51/296, 298, 302, 303; 437/225; 257/618; 427/180

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS-U.S. PATENTS TEXT SEARCH

HOLLOW(10A) MICROSPHERES AND (ABRASIVE OR GRIND? OR POLISH?)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,928,949 (WAGNER) 30 DECEMBER 1975 Figure 2, column 5, lines 20-25	1-36
Y	US, A, 4,799,939 (BLOECHER) 24 JANUARY 1989 Column 2, lines 5-15.	1-36
Y	US, A, 2,806,772 (ROBIE) 17 SEPTEMBER 1957 Figures 2 and 3.	18-23
Y	US, A, 4,927,432 (BUDINGER) 22 MAY 1990 Column 1, lines 10-40.	25, 36

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 07 September 1993	Date of mailing of the international search report 04 NOV 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer WILLIAM WATKINS
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-2351

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**